Optimization of comb-shaped polycarboxylate cement dispersants to achieve fast-flowing mortar and concrete

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ABSTRACT: Concretes and mortars possessing a low water-to-cement (w/c) ratio (<0.40) liquefied with comb-shaped polycarboxylate (PCE) copolymers commonly exhibit a sticky, honey-like consistency, and slow flow behavior. The stickiness is owed to high plastic viscosity of the suspension. In this study, different PCE comb polymers based on methacrylate ester, allyl, vinyl, and isoprenyl ether macromonomers were synthesized and analyzed. It was found that their hydrophilic–lipophilic balance (HLB) value, i.e., the balance between the hydrophilic and lipophilic parts in these PCE molecules determines their effect on the plastic viscosity of a concrete. PCE copolymers mainly composed of hydrophilic parts, i.e., such possessing high HLB values, impart low plastic viscosity. Allyl ether—maleic acid based PCEs exhibit especially high HLB values and thus impart low plastic viscosity. Higher viscosities were recorded for isoprenylether PCEs, while methacrylate-ester and vinyl ether PCEs possess particularly low HLB values and hence produce a pronounced sticky concrete. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42529.

INTRODUCTION

The invention of polycarboxylate (PCE)-based superplasticizers in 1981 in Japan started a new era in concrete plastification.[1] While such methacrylate ester (MPEG)-based superplasticizers were the first of this kind on the market, many different variations of PCEs have evolved since then. Among them are allyl ether (APEG), methallyl ether (HPEG), isoprenyl ether (IPEG or TPEG), and vinyl ether (VPEG) based copolymers.[2–4] Generally, PCE superplasticizers are comb-shaped macromolecules which are composed of an anionic backbone holding polyglycol pendants. The anionic backbone adsorbs on positively charged sites present at the surface of cement particles, thus causing dispersion of the particles which originates from a steric effect of the side chains protruding into the cement pore solution.[5] PCEs constitute powerful dispersants for concretes exhibiting very low water-to-cement (w/c) ratios (especially at <0.40). There, they greatly outperform other superplasticizers based on polycondensation technology.[6]

Applicators commonly observe that mortars or concretes which possess low w/c ratios and contain PCE superplasticizers can reach a large spread flow value in the slump flow test, thus indicating good dispersion of the mixture. However, the time to reach the final spread is very long as the mortar or concrete show a very slow and creeping flow behavior. In fact, such mortars and concretes exhibit a honey-like consistency and appear

very sticky.[7] This phenomenon becomes even more pronounced at decreasing w/c ratios. However, such rheological behavior of mortars and concretes is highly undesired in terms of pumpability, placement, and spreading in narrow formworks or in concrete elements holding densely packed steel reinforcement.[8] Furthermore, such lower concrete viscosity is also beneficial from an environmental viewpoint because the energy required to pump and compact such concrete is greatly reduced.[9] A previous study revealed that a correlation between the hydrophilic–lipophilic balance (HLB) value of a PCE and its flow behavior (time to empty) in the so-called V-Funnel test exists.[10] Yet, no correlation between the flow behavior and specific rheological parameters such as, for example, apparent and plastic viscosity or yield stress of a cement paste could be established.

The aim of the present study was to identify the rheological characteristics causing such sticky flow behavior. In particular, the effect of several PCE copolymers on yield stress and plastic viscosity of cement pastes and mortars was investigated. Based on those experiments, it was sought to understand how the chemical structure of PCEs can be optimized to achieve a fast, water-like flow behavior. For this purpose, a series of MPEG, APEG, IPEG, and VPEG based PCE copolymers were synthesized and their HLB values were calculated. Second, their overall dispersing performance was studied on mortars subjected to mini slump, V-funnel, and flow line testing. Thereafter, yield

stress and plastic viscosity of cement pastes holding those PCEs were determined using shear-rate-dependent rotational viscosimetry. Finally, the molecular properties of the PCE copolymers were correlated with their effect on the rheological parameters, and an explanation for the different flow characteristics was sought.

MATERIALS AND METHODS

Cement

The cement chosen for the experiments was an ordinary Portland cement (CEM I 52.5 N from HeidelbergCement, Geseke plant, Germany). Its C_3A content was 8.4 wt %. Therefore, it requires a relatively high dosage of superplasticizer.[11] Its phase composition as determined by quantitative X-ray diffraction (Q-XRD; instrument: Bruker axs D8, software: Topas 3.0) is shown in Table I. Average particle size (d_{50} value; laser granulometer Cilas 1064, Cilas Company, Marseille, France) of the cement sample was 12 μm and its density was 3.14 g/cm^3 (Helium pycnometer).

Chemicals

Acrylic acid, maleic anhydride, sodium persulfate, and benzoyl peroxide (all analytically pure grade) were purchased from Merck KGaA, Darmstadt/Germany. The allyl ether macromonomers α-allyl-ω-methoxy polyethylene glycol ($n_{EO} = 23$ or 34) were obtained from Nippon Oil & Fats Corporation, Tokyo/Japan, while the α-allyl-ω-hydroxy polyethylene glycol ($n_{EO} = 34$) macromonomer was provided by INEOS Group AG, Rolle, Switzerland. Methoxypolyethylene glycol ($n_{EO} = 7$, 10, or 25) was received from Clariant Deutschland GmbH, Gendorf/Germany. Low molecular weight ($M_w = 7100$ Da) polymethacrylic acid was obtained from DOW Chemical, Schwalbach/Germany. The isoprenyl ether macromonomers ($n_{EO} = 52$, 70, and 90) were received from Liaoning Oxiranchem Ltd., Liaoning, China.

Polymer Synthesis

A series of twelve PCE samples including three MPEG, four APEG, three IPEG, and two VPEG PCE copolymers were synthesized and studied.

Three MPEG-PCE copolymers (designated as MPEG-7, MPEG-10, and MPEG-25) were methacrylic acid-ω-methoxy polyethylene glycol methacrylate ester (MPEG) copolymers with side chains holding 7, 10, and 25 ethylene oxide (EO) units, respectively. Their chemical structure is displayed in Figure 1. The monomer ratios were varied to achieve a constant weight ratio of acid to ester of 25/75. This constant ratio was chosen because there, the dosages of the PCE samples in cement are almost independent of their side-chain length and produce similar flow values. This allows a better comparison of the PCE samples. The MPEG PCEs were synthesized by grafting methoxypolyethylene glycol onto a low molecular weight (7100 Da) polymethacrylic acid backbone. In a typical preparation, 25 g of polymethacrylic acid mixed with 75 g of methoxypolyethylene glycol were placed in a 250 mL round bottom flask and heated to 175°C while stirring under high vacuum (∼0.03 mbar). The reaction was finished after ∼3 h when no more gas (H_2O) release was observed. After cooling to 90°C, the colorless melt was diluted with 100 mL DI water to yield a 50 wt % aqueous

Table I. Phase Composition of the CEM I 52.5 N Sample, as Determined by Q-XRD Using *Rietveld* Refinement

Phase	Wt %
C_3S, m	67.2
C_2S, m	14.0
C_3A, c	7.2
C_3A, o	1.2
C_4AF, o	2.7
Free lime (*Franke*)	0.1
Periclas (MgO)	0.0
Anhydrite	2.4
$CaSO_4$ hemihydrate[a]	0.0
$CaSO_4$ dihydrate[a]	3.8
Calcite + quartz	4.6

[a] Determined by thermogravimetry.

PCE solution, which after cooling to room temperature was neutralized to pH 7 using aqueous NaOH solution.

Another four PCE samples designated as APEG-23, APEG-34, APEG-34-OH, and APEG-34-AM were allyl-ether-based comb polymers. Their chemical structures are also exhibited in Figure 1. Their synthesis was performed as follows: For APEG-23, APEG-34, and APEG-34-AM, 90 g of the macromonomer α-allyl-ω-methoxy poly(ethylene glycol) and for APEG-34-OH, α-allyl-ω-hydroxy poly(ethylene glycol) macromonomer containing 23 or 34 EO units, respectively, and an equimolar amount of maleic anhydride were added to a 250 mL five neck round-bottom flask, heated to 90°C and polymerized in bulk. Initiator was benzoyl peroxide and its dosage was one fifteenth of the molar quantity of the allyl ether macromonomer employed. Every 5 min, the initiator was added as powder in equal portions over a time span of 1.5 h. At the end of initiator addition, the temperature was raised to 100°C for another 1.5 h. After the reaction was completed, DI water (100 mL) was added to yield a slightly yellow, moderately viscous aqueous solution with a solid content of ∼50 wt %. The aqueous PCE solution was then cooled to ambient and its pH was adjusted to 7 using 30 wt % aqueous NaOH. Owed to the resonance stabilization of the allyl radical which does not homopolymerize, the allyl-ether-based PCEs exhibit a strictly alternating (tactical) structure of allyl ether macromonomer and maleic acid at a molar ratio of 1 : 1.[12] Sample APEG-34-AM additionally contained an equimolar amount of allyl maleate as auxiliary comonomer which greatly improves the dispersing performance.[13] The preparation of allyl maleate monomer has been described in this previous literature.

Furthermore, three IPEG PCE samples designated as IPEG-52, IPEG-70, and IPEG-90 were prepared via free radical copolymerization from acrylic acid and isoprenyl ω-hydroxy polyethylene glycol macromonomers containing 52, 70, or 90 EO units (for their structure, see Figure 1). An isoprenyl ether to acrylic acid ratio of 85 : 15 wt % was chosen for all samples, as it was found to produce PCEs with superior dispersing performance. In preparation, a 250 mL four neck round bottom flask containing ∼25 mL of DI water under a nitrogen atmosphere was
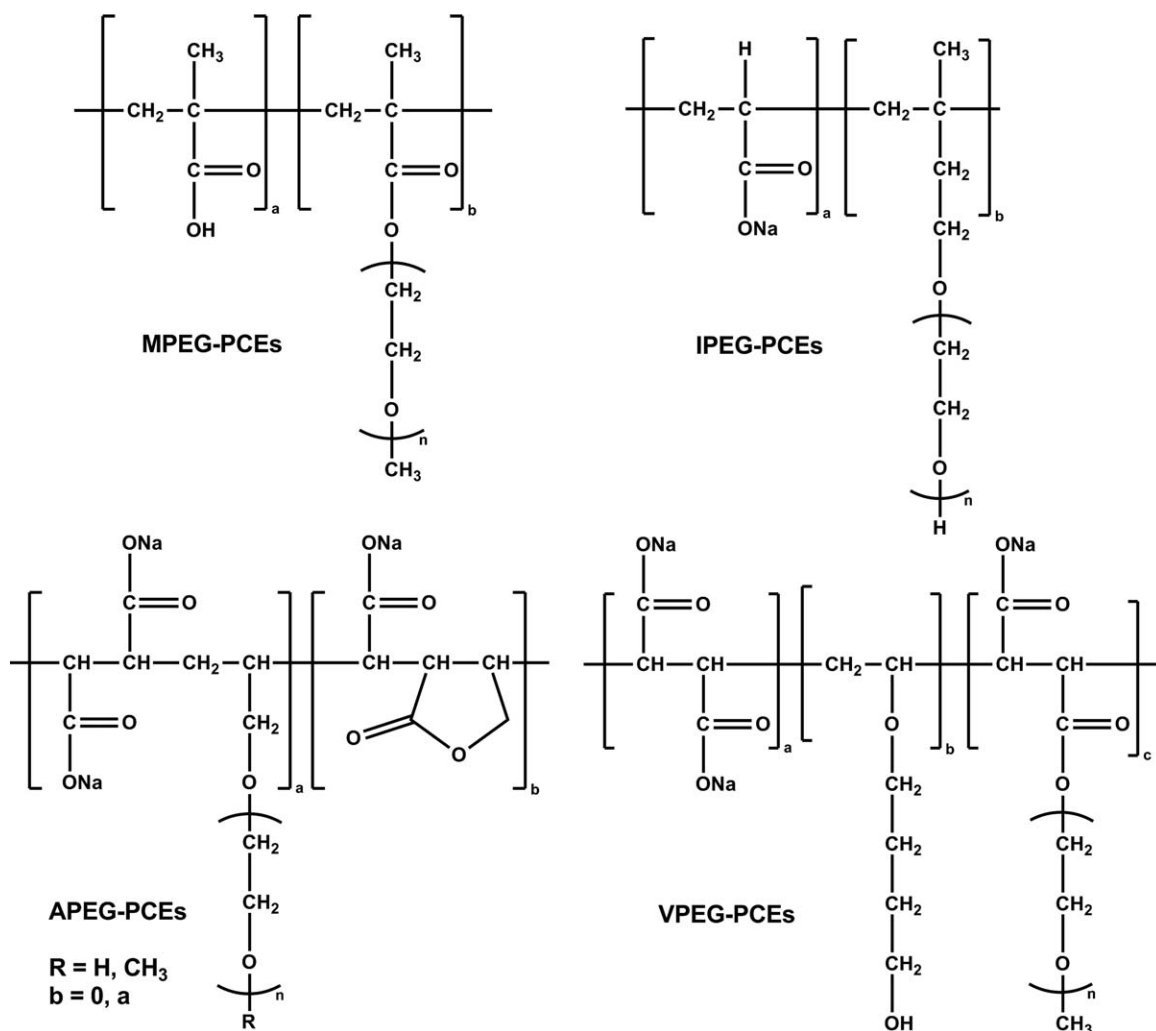
Figure 1. Chemical structures of the PCE samples synthesized.

heated to 80°C. Using peristaltic pumps, two solutions were simultaneously fed into the reactor, one containing acrylic acid (15 g), isoprenyl ether macromonomer (85 g), mercaptopropionic acid (1.0 g) as chain transfer agent and water (100 g), while the other held 1.0 g of sodium persulfate initiator dissolved in 25 mL water. The monomer solution was fed into the reactor within 3 h, while the initiator solution was added within 4 h. After cooling, the colorless polymer solutions were neutralized to pH 7 using a 30 wt % NaOH solution. The final products exhibited a solid content of ~40 wt %.

Lastly, two VPEG PCEs based on 4-hydroxybutyl vinyl ether (which enhances their compatibility with clay impurities in concrete) were synthesized as described in a previous literature.[14] The samples designated as VPEG-23 and VPEG-45 were composed of maleic acid, 4-hydroxybutyl vinyl ether, and ω-methoxypolyethylene glycol monomaleate ester at a molar ratio of 3 : 7 : 2. The maleic ester macromonomers contained 23 or 45 EO units. The general chemical structure of these PCE copolymers is exhibited in Figure 1.

All PCE samples were characterized by size exclusion chromatography (SEC) using a Waters 2695 separation module equipped

with a refractive index detector (2414 RI from Waters, Eschborn, Germany) and a three-angle light scattering detector (Dawn EOS from Wyatt Technology, Santa Barbara, CA, USA). A dn/dc of 0.135 mL/g was used to calculate their molar masses relative to polyethylene oxide.[15]

Cement Dispersion

At first, the general dispersing force of the PCE samples was determined using a "mini slump" test on the basis of DIN EN 1164 standard. The performance of a "mini slump" test is illustrated in Figure 2.

For the test, a mortar is prepared from 675 g CEM I 52.5 N, 1350 g Normsand and 202. g of H_2O (w/c = 0.30), and mixed using a ToniMIX eccentric agitator from Toni Technik Baustoffprüfsysteme GmbH, Berlin/Germany, as specified in DIN EN 196. The flow value (spread) of this mortar was 8 cm which is the diameter of the VICAT cone used for the test (height 40 mm, top diameter 70 mm, bottom diameter 80 mm), thus indicating that the mortar has no flowability. In the next step, the PCE dosages were determined which can produce a flow value of 18 ± 0.5 cm in the "mini slump" test. For this purpose, the appropriate amount of PCE polymer was dissolved in the
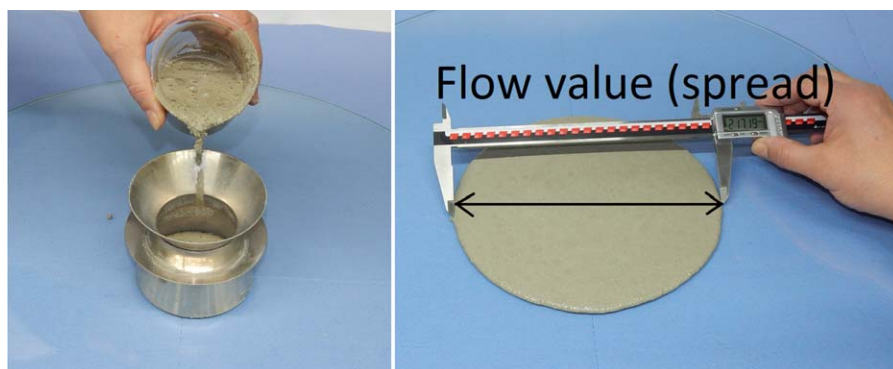
Figure 2. Performing a "mini slump" test with mortar. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixing water. After mixing, the mortar rested for 5 min to simulate actual conditions in a concrete mixing plant. Then the mortar was filled to the brim of the VICAT cone placed on top of a glass plate. The cone was vertically removed and the resulting spread was measured twice, the second being in a 90° angle to the first measurement. The average was calculated and presented as the slump flow value.

A diagram presenting the mix proportions and the steps taken in the preparation of the mortars is exhibited in Figure 3. Note that a new batch of mortar was prepared for each test performed.

Flow Line Test and Funnel Empty Times
The same mortars as prepared above for the "mini slump" tests were also evaluated in a so-called flow line according to the DIN EN 13395-2 standard to capture their flow behavior. Furthermore, the empty times of a V-funnel holding 1 L of mortar were assessed following DIN EN 12350-9 norm. Images from the experimental setup and performance of these tests are shown in Figure 4.

In both cases, the mortars were filled to the calibration mark of the devices (1 L each) and the plug was then opened. In the flow line test, the time required for the mortar to reach its final spread was determined, while in the V-funnel test, the time to empty the funnel was measured. At empty time, the period until the steady stream of mortar disrupted or when the flow stopped due to stickiness was taken.

Rotational Viscometry
A rotational viscometer (FANN 3500S from Chandler Engineering, Tulsa/Oklahoma, USA) was used to measure yield stress and plastic viscosity of cement pastes composed of 350 g CEM I 52.5 $\underline{N}$ and 105 g DI water (w/c = 0.30) following the standard API RP10 set by the American Petroleum Institute in their norm for oil well cements.[16] This mixture presents the corresponding

cement paste used before in the mortar tests. Here, PCE dosages were adjusted to achieve a 26 ± 0.5 cm flow value in the "mini slump" test using the cement paste. This addition is comparable to the dosage required in mortar to reach a flow value of 18 ± 0.5 cm. The values of yield stress and plastic viscosity were calculated according to the *Bingham* model. There, the shear stress τ depends on the yield stress τ_0, the plastic viscosity μ, and the shear rate $\dot{\gamma}$ as shown in the equation as follows:

$$\tau = \tau_0 + \mu \cdot \dot{\gamma}$$

Calculation of HLB Values for PCE Polymers
HLB values were calculated according to *Griffin's* method for macro tensides using the following formula:[17,18]

$$HLB = 20 \cdot M_h / M$$

where M_h represents the weight portion of the hydrophobic parts contained in the macro tenside and M presents the molar mass of the molecule.

The following assumptions were made for the calculations:

- 100% of the portion of polyethylene glycol present in the PCE molecule were assigned to the hydrophilic part.
- Carboxylate groups and groups located in their direct neighborhood were also added to the hydrophilic part.
- Terminal CH_3 groups and all other groups in the PCE molecule were assigned to the hydrophobic part.

As examples, the calculations for the PCE copolymers MPEG-7, APEG-34-OH, IPEG-52, and VPEG-23 are illustrated in Figure 5.
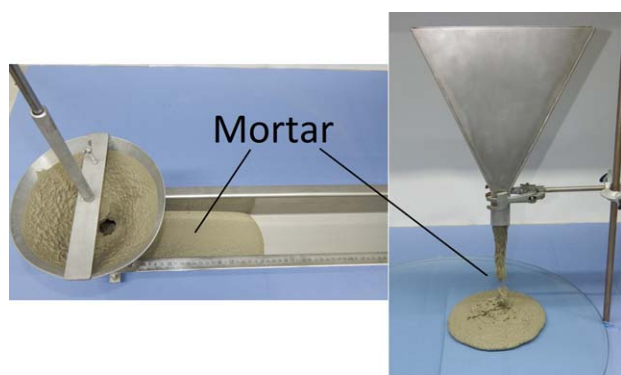
RESULTS AND DISCUSSION
Analytical Data of the Polymers
All PCE samples were characterized by SEC. Apart from the molecular weights and the polydispersity index of the polymers,
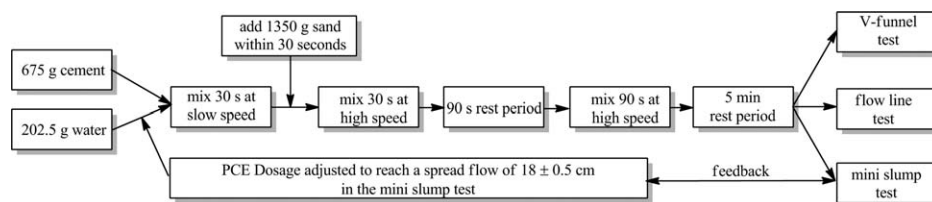
Figure 3. Mix proportions and procedure taken for the preparation of the mortars subjected to V-funnel, flow line, and mini slump testing.

Figure 4. Setup and performance of the flow line (left) and the V-funnel test (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SEC can also determine the monomer conversion. Note that in the case of the MPEG, IPEG, and VPEG PCEs, the side chains are distributed randomly along the backbone of the polymer whereas for the APEG PCEs, a strictly alternating monomer sequence occurs.[19] The analytical results are presented in Table II.

In the following, the effect of the different PCE samples on the flow behavior of cement pastes and mortars was studied applying the mini slump, flow line, and V-funnel tests. In all these tests, gravity constitutes the main force which controls the principle flow behavior, thus it was possible to interconnect the results from these different methods.

Dispersion Force of Polymers
The PCE dosages required to achieve an 18 cm slump flow from mortar in the "mini slump" test are exhibited in Table III. Obviously, all polymers tested can reach the required flow value at an economical, low dosage of <0.5% by weight of cement. The highest dosage is required for MPEG-7 (0.45%), which is owed to its short side chain and thus a weaker steric repulsion effect. The best performing superplasticizers are the IPEG type PCEs and the APEG PCE modified with allyl maleate as comonomer, while the VPEG-based PCEs perform similar as conventional APEG PCEs. This tendency is in good agreement with the results of previous studies.[20]

Flow Line Test and Funnel Empty Times
The flow line test (see Figure 4) imitates the spreading of mortar or concrete when placed in a formwork. In actual application not only the spread (i.e., how far the mortar or concrete can flow), but also the speed of flow is important because it signifies at which rate the placement of concrete can proceed and whether the concrete can reach distant corners or edges in complicated formworks. In rheological terms, the speed of flow of a suspension is linked to its plastic viscosity. This property can be measured experimentally by using rotational viscosimetry. It is well established that at medium to high w/c ratios (>0.45), the flow speeds of mortars holding PCE superplasticizers are comparable. However, the situation changes completely when mortars or concretes possessing low w/c ratios (especially <0.35) are used.

The flow behavior of mortars can be assessed in the flow line test. Here, the same mortars as applied in the "mini slump" test were studied again. It was found that all mortars produced very similar flow values of 42–45 cm, independent of the type of polymer, whereas the time required to reach this flow value (i.e., the speed of flow) was very different, depending on the chemical composition of the superplasticizer tested. Especially, the VPEG-based PCE samples exhibited a very slow, creeping flow behavior, whereas mortars holding APEG PCEs reached the final flow much faster, thus suggesting that the plastic viscosities of the mortars must be quite different. The IPEG PCE sampled showed medium flow speed, followed by the MPEG-based PCEs.

As it is quite difficult in the flow line test to accurately quantify the flow speed, the empty times from a V-funnel were looked at. This test is very common throughout the industry and therefore is specified in a DIN EN standard. All mortars tested here had the same compositions as in the "mini slump" and flow line tests (Figure 3). Here, very large differences in the speed of flow under gravity were observed for the different polymers (Figure 6). The longest times to empty were found for the two VPEG PCEs (230 and 265 s, respectively). In both cases, the funnel even did not empty completely because of the sticky consistency of the mortars. Whereas the MPEG and IPEG PCEs imparted much lower and comparable empty times of between 85 and 121 s. Mortars holding these PCEs always emptied completely from the V-funnel and appeared much more fluid. Superior performance was observed from mortars prepared with APEG PCEs. Their times to empty were significantly shorter. To be specific, polymer sample APEG-34-AM required 61 s, sample APEG-34 51 s, and polymer APEG-34-OH, the best performing PCE, 46 s only. These mortars exhibited a continuous and steady stream of flow through the funnel while in case of the mortars holding the other superplasticizers the sticky mortars were released more in increments. Additionally, it was noticed that when agitating the mortars holding APEG-PCEs by hand only a very minor force was required, suggesting that these mortars exhibited a pronounced low plastic viscosity. To confirm, shear-dependent viscosimetry of cement pastes holding these PCE samples was performed and the rheological parameters yield stress and plastic viscosity were determined.

Rotational Viscometry
For this test, cement pastes were prepared using the same low w/c ratio of 0.30 as before in the mortar tests, but the sand was omitted from the formulation. This simplification was deemed as acceptable because it is well established that the rheology of a mortar or concrete is mostly determined by the viscosity of the cement paste, as the particles there exhibit much higher surface area than sand or even gravel.[21] Thus, measurements of cement paste rheology can evidence the trends for fully formulated systems. All PCE dosages were adjusted to achieve a 26 cm spread from this paste when using the "mini slump" test and were the same as in the previous mortar tests (Table III). Measurements were performed at shear rates of 1.7, 3.4, 5.1, 10.2, 17, and $34\ s^{-1}$. From the rheograms obtained, the values for yield stress and plastic viscosity of the pastes were calculated according to the *Bingham* model (i.e., the slope of the line reflects the plastic viscosity, while the intersection with the y-axis presents the yield stress).
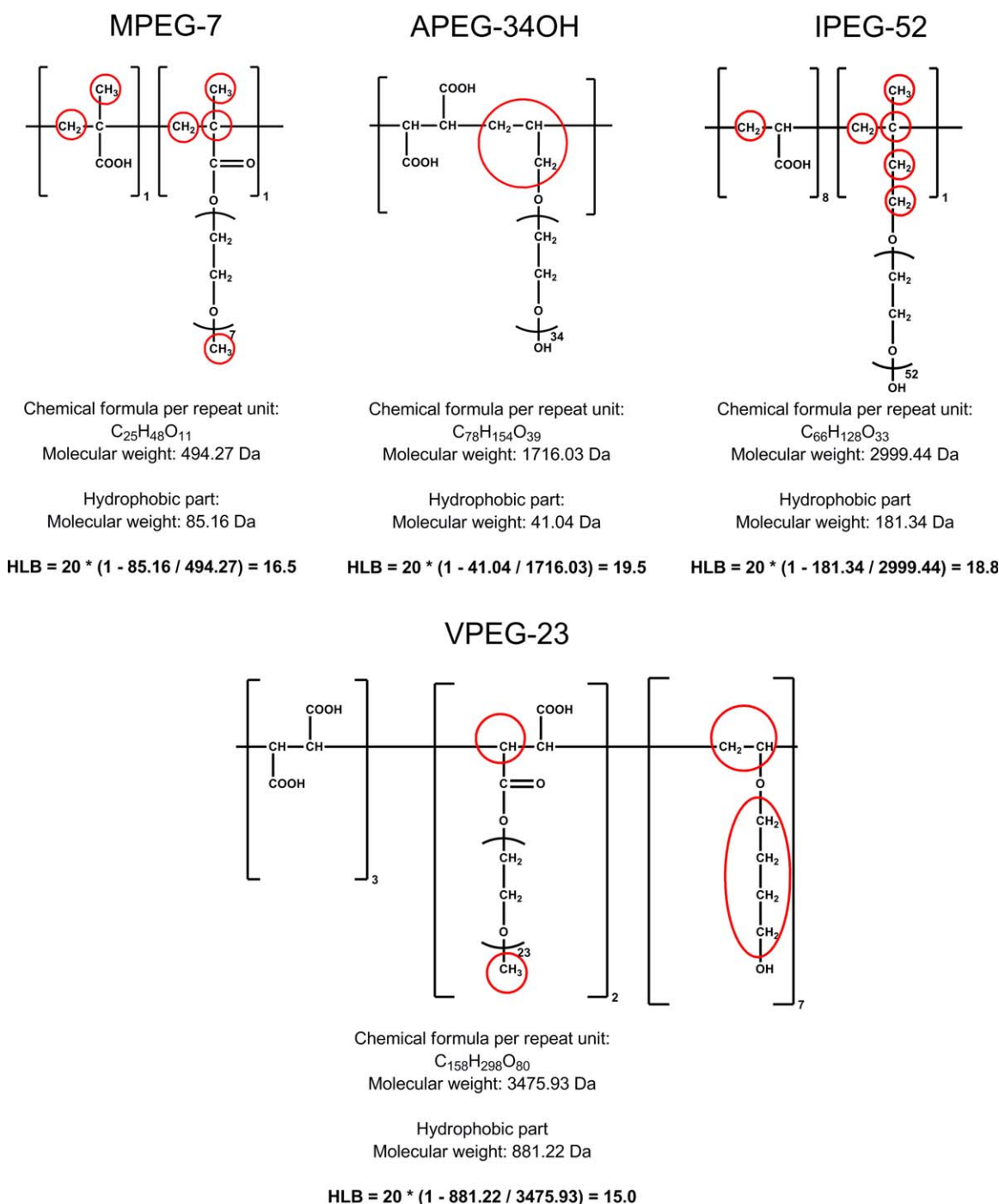
Figure 5. Examples for the calculation of the HLB values of different PCE polymers following *Griffin's* method for macro tensides; hydrophobic parts in the PCE molecules are encircled. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The rheograms are displayed in Figure 7. For clarity reason, the curves for the polymers MPEG-10, APEG-23, IPEG-50, and IPEG-90 are not shown in the figure because they were very similar to those of MPEG-25 or IPEG-52. The values obtained from the rheograms for their plastic viscosity are exhibited in Table III.

First, it becomes apparent that all cement pastes exhibit quite comparable values for the yield stress of ~5–10 Pa. This result

was expected, because all pastes were adjusted to the same spread flow of 26 cm using different PCE dosages. Note that the yield stress is a measure of how far a suspension will spread under gravitational force.[22] Second, it becomes apparent that polymers instigating a creeping and slow flow behavior in the V-funnel test always impart high plastic viscosity to the corresponding cement paste (Table III). For instance, the VPEG PCE samples producing very sticky flow exhibit values of >2000

Table II. Analytical Data of the PCE Polymers Tested

PCE polymer sample	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)	Monomer conversion (%)
MPEG-7	44,300	23,300	1.9	92
MPEG-10	59,100	27,100	2.2	90
MPEG-25	54,000	27,700	1.9	97
APEG-23	69,000	23,700	2.9	78
APEG-34	57,900	21,400	2.7	76
APEG-34OH	10,700	6,100	1.8	64
APEG-34AM	8,400	24,800	3.2	85
IPEG-52	101,200	40,100	2.5	90
IPEG-70	80,300	33,500	2.4	88
IPEG-90	81,600	32,600	2.5	82
VPEG-23	21.400	8,000	2.4	90
VPEG-45	36,400	12,500	2.9	59

Table III. Chemical Classification, Dosages, HLB Values, V-Funnel Empty Times in Mortar and Yield Stress and Plastic Viscosity of Cement Pastes Holding the PCE Samples Studied.

PCE polymer sample	Macromonomer	PCE dosage (% bwoc)	HLB value	V-Funnel empty time (s)	Yield stress (Pa)	Plastic viscosity (mPa s)
Blank	–	–	–	No flow	>100	>10,000
MPEG-7	Methacrylate ester	0.45	16.5	121	5.0	1806
MPEG-10	Methacrylate ester	0.27	16.7	100	6.1	1550
MPEG-25	Methacrylate ester	0.27	18.0	102	6.9	1388
APEG-23	Allyl ether	0.35	19.3	85	6.5	1296
APEG-34	Allyl ether	0.36	19.4	51	4.1	1146
APEG-34OH	Allyl ether	0.36	19.5	41	5.2	1089
APEG-34AM	Allyl ether	0.18	19.6	61	6.3	1130
IPEG-52	Isoprenyl ether	0.18	18.8	85	7.7	1275
IPEG-70	Isoprenyl ether	0.19	18.8	110	7.1	1354
IPEG-90	Isoprenyl ether	0.20	18.9	100	6.9	1298
VPEG-23	Vinyl ether	0.38	15.0	264	7.2	2440
VPEG-45	Vinyl ether	0.33	16.7	235	5.8	2130

mPa s for the plastic viscosity while the APEG polymers which can provide fast flow show values of 1000–1150 mPa s only. Apparently, since PCE polymers do not interact much with
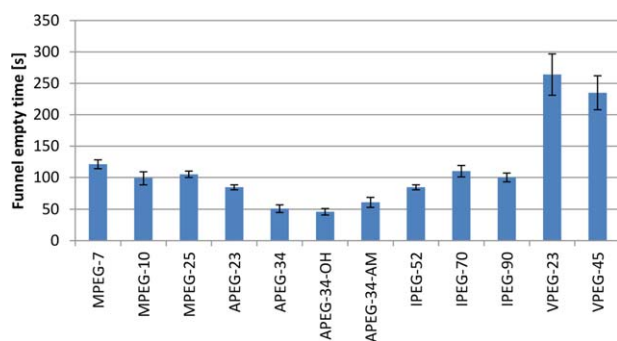

Figure 6. V-Funnel empty times of mortars holding different PCE samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sand a direct correlation between the speed of flow of a mortar and the plastic viscosity of its corresponding cement paste exists.

To confirm the observation of concrete workers that sticky flow can be observed only at low w/c ratios, the same tests were repeated at the higher w/c ratio of 0.50. In this case, all superplasticizer samples produced comparable and low values (140–160 mPa s) for the plastic viscosity of the cement pastes. This result confirms that mortars or concretes prepared at a higher w/c ratio always exhibit a high speed of flow, independent of the type of superplasticizer added. Note that the plastic viscosity of a cement paste decreases by a factor of 10 when increasing the w/c ratio from 0.30 to 0.50 while maintaining the same yield stress of ~5–10 Pa adjusted with PCE superplasticizer.

Mechanistic Study

Still, the question remained why different PCE molecules could affect the flow behavior of the cement paste in such different
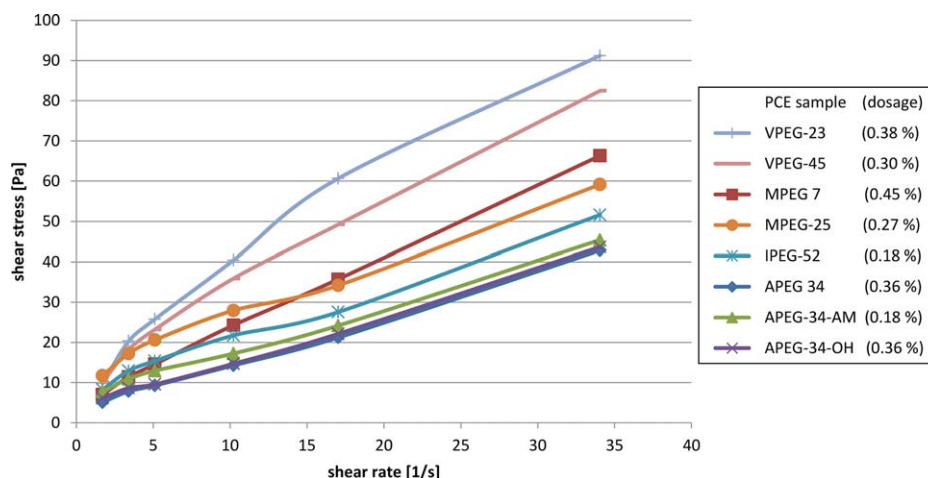
Figure 7. Rheograms of cement pastes prepared from CEM I 52.5 N (w/c = 0.30) and various superplasticizer samples (dosages by weight of cement). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

manner. It was hypothesized that the affinity of a PCE molecule to water (i.e., its overall hydrophilic character) could present the key factor which determines its effect on the plastic viscosity of a mortar or concrete. Generally, PCEs are macro tensides because in their structure they combine hydrophilic groups such as carboxylate (COO^-), hydroxy (–OH), or ethylene oxide units ($-CH_2-CH_2-O-$) with hydrophobic groups (i.e., $-CH_2-$, $-CH_3$).

According to Griffin's method, the HLB values of macro tensides can be derived from their chemical structure. This calculation was performed for all PCEs tested in mortar. For some selected PCE samples, the calculation method is exemplified in Figure 5. The HLB values obtained for the PCE polymers are presented in Table III. From the data, a direct correlation between the HLB value of a PCE molecule and the plastic viscosity of cement paste or the flow speed of the corresponding mortar can be established. Obviously, PCE molecules possessing high HLB values (18–20) produce fast flowing mortars characterized by low plastic viscosity, whereas PCE samples exhibiting low HLB values (15–18) instigate a creeping, sticky and slow flow behavior. Therefore, MPEG-PCEs possessing short side chains (i.e., they contain a higher portion of terminating hydrophobic $-CH_3$ groups than PCEs exhibiting longer side chains) and the VPEG PCEs which contain a large amount of hydrophobic 4-hydroxybutyl vinyl ether exhibit low HLB values and are undesirable when fast flowing mortars or concretes are to be formulated.

CONCLUSIONS

PCE superplasticizers present highly potent dispersants for concretes and mortars, even at particularly low water-to-cement ratios. Yet, apart from good particle dispersion and low yield stress, only a few PCE polymers can induce a low plastic viscosity to the system which provides a fast speed of flow. Here, it was found that only PCE polymers exhibiting a high HLB value are suitable to reduce the plastic viscosity of those systems significantly. To achieve a PCE with a high HLB value, the hydrophobic parts in the polymer such as $-CH_3$ in the backbone or the macromonomer should be avoided. For example, using acrylic or

maleic acid instead of methacrylic acid, or –OH instead of $-CH_3$ terminated macromonomers in the synthesis provides a successful route to achieve PCE products which can provide mortars or concretes of low water content with faster spreading in difficult molds and congested formworks. Furthermore, the pumping energy is reduced, making concrete placement more economical and environmentally friendly. Considering that nowadays no less than 30 billion tons of concrete are produced every year of which ~10% are high strength concrete mixed at low w/c ratios, the impact of improved transport and flow behavior of such concretes is significant.

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